EPA's Report on the Environment

Technical Documentation

Identification

1. Indicator Title

Ambient Concentrations of Selected Air Toxics

2. ROE Question(s) This Indicator Helps to Answer

What are the trends in outdoor air quality and their effects on human health and the environment?

3. Indicator Abstract

This indicator presents trends in ambient concentrations of eight air toxics across the U.S. The temporal coverage for the indicator trends depends on the availability of ambient air monitoring data. For six of the air toxics, air quality trends are depicted from 2003 to 2013; for the other two, trends are shown from 2005 to either 2012 or 2013. These time frames were selected based on application of objective site selection criteria. By tracking ambient air concentrations of air toxics—pollutants that are known or suspected to cause cancer or other serious health effects—this dataset can be used to assess how air quality may be affecting human health.

4. Revision History

July 2012: Draft indicator developed
November 2014: Indicator updated

Data Sources

5. Data Sources

The air toxics data used in this indicator were collected from the National Air Toxics Trends Station (NATTS) Network, the Urban Air Toxics Monitoring Program, and data supplemented by other state, local, and tribal air quality monitoring sites where pollutants were consistently measured between 2003 and 2013.

This indicator is based entirely on ambient air monitoring data retrieved in November, 2014, from EPA’s Ambient

Monitoring Archive (AMA), Phase IX, for hazardous air pollutants (HAPs). The AMA for HAPs is an archive of ambient HAP measurements from 1973 to 2013 and is compiled from various sources including EPA's Air Quality System (AQS), the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, and special monitoring studies. In total, the AMA for HAPs includes data from 14 data sources, with more than 90 percent coming from AQS. More information on how the AMA for HAPs was constructed is at: https://www3.epa.gov/ttnamti1/files/toxdata/techmemo2016.pdf (29 pp, 245K).

6. Data Availability

This indicator presents ambient concentrations trends for the following eight air toxics: formaldehyde, benzene, carbon tetrachloride, acetaldehyde, 1,3-butadiene, arsenic, tetrachloroethylene, and hexavalent chromium. The arsenic trends are based on sampling of particulate matter with aerodynamic diameters of 10 microns or smaller (PM_{10}), and the hexavalent chromium trends are based on sampling of total suspended particulate (TSP).

The complete set of monitoring data used to prepare trends in this indicator was queried from the annual output files from EPA's AMA for HAPs, Phase IX, which is publicly available at: http://www3.epa.gov/ttn/amtic/toxdat.html#data. The output files were further processed according to the site selection criteria and data processing methodology described below. More information about the AMA for HAPs can be found at https://www3.epa.gov/ttnamti1/files/toxdata/techmemo2016.pdf (29 pp, 245K). Further, spreadsheets have been developed to document how data were compiled for the eight pollutants displayed in this indicator. These spreadsheets provide extensive detail on the individual monitoring sites and their concentration trends. The spreadsheets can be accessed from the following links:

- Acetaldehyde (MS Excel)
- Arsenic (MS Excel)
- Benzene (MS Excel)
- 1,3-Butadiene (MS Excel)
- Carbon tetrachloride (MS Excel)
- Formaldehyde (MS Excel)
- Hexavalent chromium (MS Excel)
- Tetrachloroethylene (MS Excel)

For the selected air toxics, trends are reported as far back as 2003, even though some monitoring data are available for earlier years. Choosing the time horizons for the ambient concentration indicators is a matter of balance. There is a desire to present data for as many years as possible. However, doing so comes at the expense of the number of sites with sufficient data. The starting points used in the air toxics indicator are based on an analysis of how far back the trend analysis could reasonably go while still having a large set of trend sites that still meet the site selection criteria described below.

Methodology

7. Data Collection

Study Design

This indicator was developed to present concentration trends for the air toxics—or hazardous air pollutants (HAPs)—that accounted for the greatest amount of estimated incremental cancer risk attributed to breathing outdoor air pollution based on data published in the 2005 National-Scale Air Toxics Assessment (NATA) (U.S. EPA, 2011) and in a peer-reviewed publication (McCarthy et al., 2009). The following 10 pollutants accounted for 91.7 percent of the estimated incremental cancer risk that is attributed to inhalation exposure to outdoor air pollutants, according to the 2005 NATA:

- Formaldehyde (45.1 percent of estimated nationwide risk attributed to outdoor air quality)
- Benzene (14.9 percent)
- Acetaldehyde (6.7 percent)
- Carbon tetrachloride (5.7 percent)
- Naphthalene (4.6 percent)
- 1,3-Butadiene (3.9 percent)
- Polycyclic aromatic hydrocarbons (PAH)/polycyclic organic matter (POM) (3.1 percent)
- Chromium compounds (2.8 percent)
- Arsenic compounds (2.7 percent)

- Tetrachloroethylene (2.2 percent)

Sufficient data are available to develop concentration trends for eight of these 10 pollutants. The two exceptions are naphthalene and PAH/POM. Naphthalene is not included in this indicator because widespread measurement at air monitoring stations did not occur until 2008 or 2009 at most NATTS monitoring stations, and PAH/POM is not included because it represents a group of pollutants and not an individual pollutant. The remaining eight pollutants account for 84.0 percent of the total estimated incremental nationwide cancer risk attributed to exposure to outdoor air pollution.

The ambient air monitoring data used to develop this indicator are based on observations where the pollutants were measured using methods employed by the NATTS, PAMS, and selected state networks. For example, volatile organic compound (VOC) samples collected under the NATTS network are analyzed using EPA Compendium Method TO-15. For sites using the National Contract, these monitoring results are labeled with an AQS method code of "101" to designate that samples were collected using "Canister Subambient Pressure" and were analyzed using "Multi-Detector Gas Chromatograph (GC)." For sites not using the National Contract, the AQS method codes are typically "176," which refers to samples collected using "6 liter subatmosphere stainless steel canister" and analyzed by "ENTECH preconcentrator gas chromatograph and mass spectrometry (GC/MS)."

The NATTS network was designed to generate long-term air quality trend data for HAPs of consistent quality. This network includes monitoring sites from urban, suburban, and rural settings, with the number of monitoring sites varying across the selected pollutants based on availability of monitoring data. The majority of monitoring stations are located in urban environments where emissions sources and populations are also most concentrated. The concentrations of the air toxics are considered temporally and spatially representative across the United States because the ambient concentration trend of each pollutant is a composite of a large number of trend sites. To qualify for inclusion in the trend analyses, monitoring must take place at the sites over the trend years. The NATTS monitoring network is not designed to represent sensitive populations or ecosystems.

As stated above, in addition to the NATTS sites, the indicator includes data from other sites with that measured air toxics using comparable methods but were not part of the NATTS network. The data spreadsheets listed in Data Availability specify the networks to which each monitor belongs. The non-NATTS sites are found throughout the country, and monitoring is being conducted at these sites for various reasons. All data from AQS were used to select monitoring sites. Any sites from other networks (e.g., Photochemical Assessment Monitoring Stations [PAMS], Urban Air Toxics Monitoring Program stations) with data that met the completeness criteria are therefore also included in the indicator.

Sampling and Analytical Methods

Ambient concentrations for the pollutants selected in this indicator are measured using standard sampling and analytical methods. The data spreadsheets listed in Data Availability specify the sampling and analytical methods used at each monitoring site. For most of the air toxics selected for display in this indicator, these methods determine ambient air concentrations over a 24-hour period. For a small portion of the benzene and 1,3-butadiene data (i.e., measurements from fewer than 10 percent of the monitoring sites), sub-daily duration sampling does occur. The measurements supporting this indicator generally were collected with one of the following methods, with the specific method depending on the chemical form of the pollutant being sampled:

- EPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (see http://www3.epa.gov/ttn/amtic/files/ambient/airtox/tocomp99.pdf (PDF) (37 pp, 166K)). Methods in this compendium were used to measure the volatile organic compounds and carbonyls covered by this indicator.
- EPA's Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air (see http://www3.epa.gov/ttn/amtic/files/ambient/inorganic/iocompen.pdf (PDF) (21 pp, 189K)). Methods in this compendium were used to measure arsenic concentrations presented in this indicator.
- A modified version of a method developed by the California Air Resources Board (see http://www3.epa.gov/ttnamti1/files/ambient/airtox/hexchromsop.pdf (PDF) (19 pp, 69K)). This method was used to measure the hexavalent chromium concentrations presented in this indicator.

These methods have undergone extensive independent peer review and, when applied correctly, are widely viewed as providing scientifically valid measurements. Additional information about ambient air monitoring can be found at http://www3.epa.gov/ttn/amtic/.

In some cases and as noted previously, data collected with different methods were considered. For example, the benzene trend for the NATTS site in Phoenix, Arizona, includes data collected using two methods. In early 2004, this site had samples analyzed under the National Contract, and thus the VOC analyses were conducted according to AQS method code 101. However, later in 2004, site operators began using a different laboratory for the VOC analyses, and

the AQS method code changed to 210, which designates sampling in a 6-liter pressurized canister and analysis using a "Cryogenic Precon" GC/MS. These methods both follow the procedures of the overarching EPA Compendium Method TO-15. As another example, the formaldehyde trend for the NATTS site in Northbrook, Illinois, includes data collected using two methods. In 2003 and 2004, samples were collected in absorbent cartridges coated with 2,4-dinitrophenylhydrazine and analyzed using high performance liquid chromatography with an ultraviolet absorbent detector. This site's sampling apparatus was then equipped with a denuder coated with potassium iodide to minimize negative interferences from ozone, which have been reported as being in the range of 5.6 to 7.7 percent for formaldehyde (e.g., Ho et al., 2013).

Method differences were not considered as part of this indicator, and have not been considered in previous iterations of this indicator. It was assumed that there are no significant biases across methods that will change the overall indicator trends. The spreadsheets listed in Data Availability fully document all methods used at the monitoring sites included in this indicator.

Documentation

Ambient air monitoring data for air toxics have been extensively documented. Many documents are available through EPA's Ambient Monitoring Technology Information Center (AMTIC), an online clearinghouse that provides links to numerous resources that describe sampling and analytical methods for air toxics (see http://www3.epa.gov/ttn/amtic/airtox.html). The data spreadsheets listed in Data Availability provide extensive information on how this indicator's data were downloaded and processed. For every monitoring site selected, these spreadsheets also document the sampling and analytical methods used, the frequency and duration of sampling, the number of non-detect observations, and other important details. Other general information on air toxics monitoring programs and procedures can be found at:

- The NATTS sampling work plan (http://www3.epa.gov/ttnamti1/natts.html)
- Air monitoring methods (http://www3.epa.gov/ttnamti1/airtox.html)
- Quality assurance procedures (http://www3.epa.gov/ttnamti1/airtoxqa.html)

8. Indicator Derivation

Several data processing steps were employed to generate the trend exhibits presented in this indicator from the ambient air monitoring data originally downloaded from EPA's AMA for HAPs, Phase IX. The first step in the data processing was to determine if a given site's monitoring data should be included in the indicator in the first place. Only those monitors with sufficient data to characterize trends were included, and this determination was based on whether the data supported reliable calculation of annual average concentrations.

For the overwhelming majority of sampling results considered in this indicator, sites operated with 24-hour average samples collected once every 6 days or once every 12 days. The primary exception for sample duration is that a small portion of benzene and 1,3-butadiene samples are sub-daily measurements. The data spreadsheets listed in Data Availability document the sample frequency and duration for every pollutant and monitoring site. Consistent with approaches used in other outdoor air quality trend assessments, monitoring stations were required to have at least 75 percent data completeness in order to calculate an annual average concentration for a given calendar year. Further details on these calculations are provided below. This approach was used to determine the specific calendar years for which a given site has sufficient data for calculating annual average concentrations.

Once the complete set of annual average concentrations was generated, only those sites with enough annual average concentrations over the trend horizon were included in the indicator. More specifically, for six of the eight pollutants considered, the trend horizon was 2003-2013. For these pollutants, a site was required to have valid annual averages for at least 9 of the 11 years in the 2003-2013 time frame. Further, sites with two consecutive years without valid annual average concentrations were excluded from the analysis; and sites were also excluded from this analysis when they had missing data for both the beginning and ending years in the period of record. For hexavalent chromium, the indicator includes only those sites that had at least 6 valid annual average concentrations in the 2005-2012 time frame. For arsenic, the indicator includes only those sites that had at least 7 valid annual average concentrations in the 2005-2013 time frame.

Some trend sites that met the site selection criteria had one or two non-consecutive years of "missing data" for their annual average concentrations (e.g., there may have been a year with not enough samples to calculate an annual average concentration). In these cases, missing annual mean concentrations during the trend period were filled using interpolation or extrapolation. If an end-year was missing, the concentration value from the adjacent year was used to extrapolate its value. If a central year was missing, the two adjacent years' concentrations were averaged to interpolate its value. Interpolation and extrapolation of data is an accepted method of filling in missing years when data are

missing for a site, and this approach has routinely been used in compiling EPA's air quality trends reports. The interpolation and extrapolation of data were not expected to affect the magnitude and direction of the overall concentration trends.

Some monitoring sites were equipped with more than one monitor that measured the same pollutant. This is typically tracked in AQS by the parameter occurrence code (POC). For any given pollutant and year, the POC-method combination with the most samples and highest data completeness was selected for the trend analysis. This data processing approach was not expected to affect the magnitude and direction of overall concentration trends given that the monitoring data from these sites were collected with robust methods.

Another data processing step used before generating annual average concentrations was addressing non-detect observations. Non-detect observations were replaced with a concentration of zero before computing annual averages. In some cases, the analytical laboratory or reporting agency that submits ambient air monitoring data to AQS replaces non-detect observations with surrogate values before reporting these data. Those instances were identified by searching for instances where large numbers of sampling results were replaced with the same surrogate value (e.g., zero, one-half the detection limit, the detection limit), and the surrogate values originally reported to AQS were then replaced with zero. The pollutant-specific data spreadsheets listed in Data Availability specify the numbers of non-detect observations at every monitoring site and every year of record.

All concentrations reported in this indicator are in units of micrograms per cubic meter ($\mu g/m^3$). Descriptive statistics in the indicator plots include the mean, median, 10^{th} percentile, and 90^{th} percentile concentrations for each pollutant based on the annual average concentrations calculated for the individual trend sites. EPA prepared the AMA for HAPs concentration data as local conditions, where applicable. Approximately 99.7 percent of the original concentration data from the AMA for HAPs from 2003 to 2013 were in local conditions, either as reported from the original data source or converted using local temperature and pressure.

9. Quality Assurance and Quality Control

The quality assurance/quality control (QA/QC) of the national air monitoring program has five major components: the data quality objective process, the reference and equivalent methods program, EPA's National Performance Audit Program, system audits, and network reviews (http://www3.epa.gov/ttn/amtic/netamap.html). Further information on QA/QC procedures is available through EPA's *Quality Assurance Handbook,* EPA/454/R-98/004, Section 15 (see http://www3.epa.gov/ttnamti1/qalist.html).

In addition, each state or local agency operating an ambient air monitor for EPA's monitoring networks has a quality assurance project plan (QAPP). These QAPPs must meet EPA's *Requirements for Quality Assurance Project Plans,* EPA QA/R-5 (U.S. EPA, 2001). The QAPPs for specific sites are publicly available by request to the reporting agency or the corresponding EPA Regional Office. Some QAPPs can be accessed online (see http://www3.epa.gov/ttn/amtic/plans.html). For example, the California Air Resources Board QA manual is available at http://www.arb.ca.gov/aaqm/qa/qa-manual/qa-manual.htm. QAPPs are audited at least once every 3 years as required in 40 CFR 58, Appendix A, Section 2.5.

Analysis

10. Reference Points

Unlike the criteria pollutants, no National Ambient Air Quality Standards are in effect for air toxics, and there is no consensus on which metric to use to reflect the state of the environment relative to these pollutants. However, risk assessors frequently use unit risk estimates (UREs) to estimate theoretical cancer risks associated with lifetime exposure to ambient air concentrations of air toxics. A theoretical cancer risk is calculated by multiplying the average air toxics concentration by the URE. Different health and environmental agencies have adopted different sets of URE values. The EPA Office of Air Quality Planning and Standards' most recent health criteria data, including the UREs, are documented at http://www.epa.gov/fera/dose-response-assessment-assessing-health-risks-associated-exposure-hazardous-air-pollutants and these values are updated periodically as health assessments are completed. Further information on UREs and their use is available from documentation for the National-Scale Air Toxics Assessment (https://www.epa.gov/national-air-toxics-assessment/2005-national-air-toxics-assessment).

11. Comparability Over Time and Space

This indicator's data characterize trends in the distributions—the 10^{th}, 50^{th}, and 90^{th} percentiles—of annual average

concentrations of air toxics at selected monitoring sites with sufficient data to support trend assessment. Because consistent methods were used to sample air and to process data, the distributions shown for a given pollutant are comparable from one year to the next. However, these distributions only reflect air toxics levels at the collection of monitoring sites that met the site selection criteria. The monitoring sites' locations are specified in the data spreadsheets listed in Data Availability. Nationwide trends in the distributions of average concentrations do not necessarily reflect trends at individual monitoring sites.

12. Sources of Uncertainty

Uncertainties in the indicator include spatial uncertainty from different sets of monitors for each pollutant, urban bias based on the location of most monitors, and measurement uncertainties for the measurement techniques of each of the eight pollutants, primarily with regard to the method detection limits (MDLs). Sources of uncertainty associated with the MDL include the number of sample values reported at or below the MDL and the algorithm used to process those observations (e.g., substitute with concentrations of zero or replace with concentrations of one-half the detection limit). For this indicator, a protocol was in place to consistently treat data at or below the MDL that had been censored to minimize uncertainty, as described in the Indicator Derivation section of this form. It is also noted that the instrumental measurement uncertainty on each value above the MDL is not reported in the AQS database. Therefore, quantitative estimates of instrumental uncertainty could not be included in these analyses.

13. Sources of Variability

The concentrations of the eight air toxics included in this indicator may be influenced by season, meteorological conditions, and emissions sources, contributing to the temporal and spatial variability of the pollutants. Measurement data were aggregated to annual averages and multiple years of data were used to smooth out any short-term temporal variation and enhance the long-term trend signal. Spatial variability will be smoothed by the inclusion of data from large numbers of trend sites representing a wide selection of places across the United States.

14. Statistical/Trend Analysis

The indicator presents a time series of concentrations averaged across multiple monitoring stations. No special statistical techniques or analyses were used to characterize the long-term trends and their statistical significance.

Limitations

15. Data Limitations

Limitations to this indicator include the following:

1. The data summarized in this indicator are based on the subset of monitoring sites with sufficient data over the period of record for the individual pollutants. These monitoring sites are primarily (but not exclusively) located in urban areas.
2. The indicator presents trends for the eight air toxics that account for a majority of the estimated nationwide incremental cancer risk attributed to outdoor air pollution emitted from sources of outdoor origin and with data available to characterize trends. Many additional air toxics are commonly found in outdoor ambient air.
3. To ensure that long-term trends are based on a consistent set of monitoring sites, selection criteria were applied to identify the subset of air toxics monitoring sites with sufficient data to assess trends over the period of record. Monitoring sites without sufficient data are not included in the trend analysis. Nationwide trends in the distributions of average concentrations do not necessarily reflect trends at individual monitoring sites or at locations where monitoring has not occurred.
4. Measured concentrations below the detection limits were used as reported; and non-detect observations were replaced with concentrations of zero in the trend analysis, introducing some uncertainty into the calculated trends, particularly for the 10 th percentiles shown in the exhibits. Uncertainty in trends is greatest for the pollutants with the highest proportion of data below detection.

References

Ho, S.S.H., H.S.S. Ip, K.F. Ho, W.T. Dai, J. Cao, and L.P.T. Ng. 2013. Technical note: Concerns on the use of ozone scrubbers for gaseous carbonyl measurements by DNPH-coated silica gel cartridge. Aerosol and Air Quality Research 13:1151-1160. http://aaqr.org/VOL13_No4_August2013/1_AAQR-12-11-TN-0313_1151-1160.pdf (PDF) (10 pp, 292K).

McCarthy, M.C., T.E. O'Brien, J.G. Charrier, and H.R. Hafner. 2009. Characterization of the chronic risk and hazard of hazardous air pollutants in the United States using ambient monitoring data. Env Health Pers 117(5):790-796. http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2685843/.

U.S. EPA (United States Environmental Protection Agency). 2012. Our nation's air: Status and trends through 2010. EPA/454/R-12/001. https://nepis.epa.gov/Exe/ZyPDF.cgi/P100E174.PDF?Dockey=P100E174.pdf (PDF) (32 pp, 2.5MB).

U.S. EPA. 2011. 2005 national-scale air toxics assessment. Accessed April 25, 2012. http://www3.epa.gov/ttn/atw/nata2005/.

U.S. EPA. 2001. EPA requirements for quality assurance project plans. EPA/240/B-01/003. https://www.epa.gov/sites/production/files/2016-06/documents/r5-final_0.pdf (PDF) (40 pp, 149K).

U.S. EPA. 1981. Intra-Agency Task Force report on air quality indicators. EPA/450/4-81/015.